

AD-A096 886

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MAGNETIC ORDERING IN OXIDE SOLID SOLUTIONS.(U)
MAR 81 A K CHEETHAM

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AFOSR-79-0120

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(18) (19) REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. Report Number EDARD-TR-81-1	2. Govt Accession No. AD-A096886	3. Recipient's Catalog Number
4. Title (and Subtitle) (6) MAGNETIC ORDERING IN OXIDE SOLID SOLUTIONS.		5. Type of Report & Period Covered (9) Interim Scientific Rept. 1 Sep 1979 - 31 Aug 1980
(2)		6. Performing Org. Report Number
7. Author(s) (10) A. K. Cheetham	8. Contract or Grant Number AFOSR-79-0120	(12) 7
9. Performing Organization Name and Address Chemical Crystallography Laboratory University of Oxford 9 Parks Road Oxford OX1 3PD, UK	10. Program Element, Project, Task Area & Work Unit Numbers 61102F (16) 2301/D1 (17) 02	
11. Controlling Office Name and Address European Office of Aerospace Research and Development/LNC Box 14 FPO New York 09510	12. Report Date (11) 13 Mar 1981	
14. Monitoring Agency Name and Address	13. Number of Pages 5	
15.		
16. & 17. Distribution Statement Approved for public release; distribution unlimited		
18. Supplementary Notes		
19. Key Words Magnetic ordering, metal oxides, neutron diffraction, solid solutions.		
20. Abstract → Powder neutron diffraction, magnetic susceptibility and Mössbauer spectroscopy are being used to investigate solid solutions based upon MnO, FeO, CoO and NiO. During the last twelve months, we have completed measurements on NiO-CoO and MnO-CoO, and made preliminary studies in the systems NiO-MnO, FeO-MnO and FeO-CoO. In each system we have examined the changes of spin direction and crystal symmetry as a function of temperature and pressure in the antiferromagnetic phases. The results so far suggest that the strength of the magnetic anisotropy associated with the metal ions falls in the sequence $\text{Co}^{2+} > \text{Mn}^{2+} \gg \text{Fe}^{2+} \sim \text{Ni}^{2+}$. This order is unexpected and we are carrying out further experiments and calculations in order to obtain a better understanding of the interactions in these systems.		

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Magnetic Ordering in Oxide Solid Solutions

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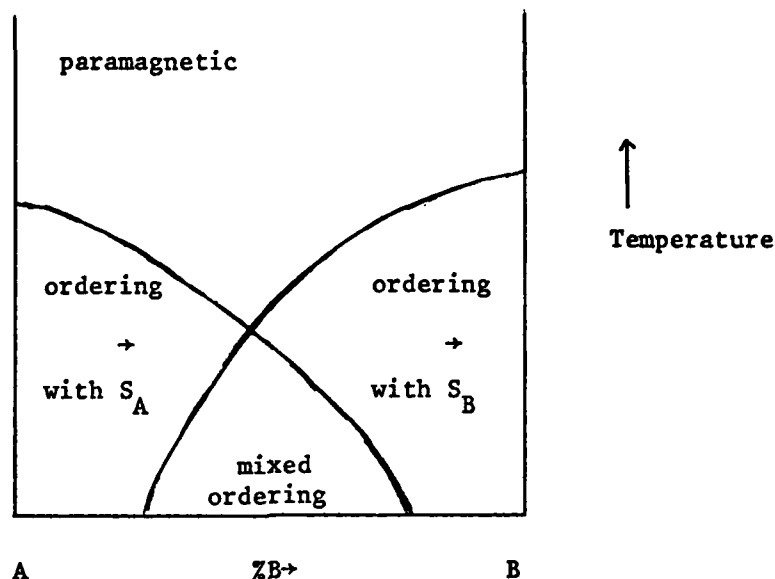
Sections 1, 2 and 3 describe the background to this work and sections 4 - 9 summarise the results we have obtained with AFOSR support during the first year of our grant (1979/80).

1. Magnetic ordering in transition metal oxides has been extensively studied by susceptibility and neutron diffraction techniques and the nature of the magnetic interactions in systems containing one type of paramagnetic ion is well understood. Ternary oxides containing more than one type of cation site (e.g. spinels) have also received much attention and the origins of their magnetic properties are again well known. We are presently focusing our attention on the magnetic ordering characteristics of some simple oxide solid solutions in which the two paramagnetic ions occupy the same type of site, but have competing anisotropies. These are solid solutions of the first transition series monoxides MnO, FeO, CoO and NiO; they adopt the sodium chloride structure. Our results will have implications for the magnetic behaviour of a wide range of materials.

2. Neutron diffraction studies on MnO and NiO have shown that they undergo rhombohedral distortions ($\alpha > 60^\circ$) below their Néel temperatures and in each compound the spin direction is within the (111) plane.¹ On the other hand, CoO exhibits a tetragonal distortion with the spin tilted 27.4° away from the unique axis.² Ferrous oxide is non-stoichiometric and we have recently examined the influence of defect clustering upon its magnetic properties;³ its symmetry is rhombohedral and the spins point along the [111] axis.

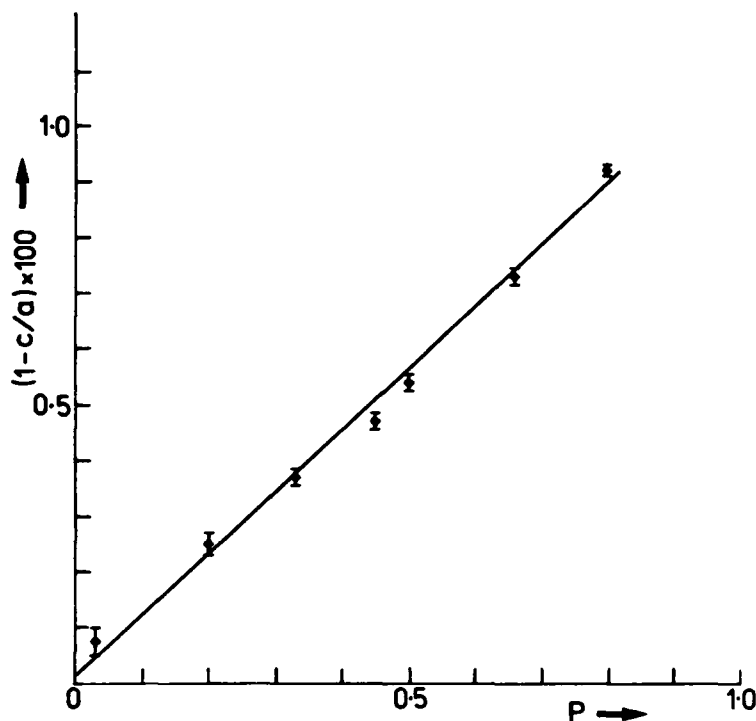
3. The first row monoxides are known to form solid solutions, but the effect of the ensuing disorder upon the magnetic structure has not been investigated

experimentally. This problem is of current theoretical interest and renormalisation group calculations have recently been reported for several types of disordered systems.⁴ The results of a treatment for systems containing spin with competing anisotropies is shown below:



4. During the first year of our AFOSR low-cost grant, we have completed measurements on the NiO-CoO system and obtained interesting preliminary results on MnO-CoO, MnO-NiO, MnO-FeO and CoO-FeO. We have secured substantial allocations of time on the high resolution powder diffractometer D1A at the high flux beam reactor in Grenoble. Our experiments have shed new light on the magnetic anisotropies of transition metal ions in mixed metal oxides and have also yielded new information about the defect structure of solid solutions based upon non-stoichiometric ferrous oxide.

5. In the system NiO-CoO, we have analysed data at several compositions by profile analysis techniques.⁶ The magnitude of the observed magnetic moments indicates that the spins are collinear at all compositions and in the range CoO-Co_{0.10}Ni_{0.90}O, the spin direction remains the same as that in CoO itself. This remarkable observation reflects the very strong single ion anisotropy of Co²⁺, an effect which is also apparent in the linear dependence of the tetragonal c/a ratio upon the mole fraction, P, of CoO:



Refinements on a sample of composition $\text{Co}_{0.05}\text{Ni}_{0.95}\text{O}$ show that the spin makes an angle of 33° with $[001]$, intermediate between CoO and NiO , and a small monoclinic distortion of the unit cell arises from the superposition of both rhombohedral and tetragonal symmetry. Molecular field methods have also been used to calculate the temperature dependence of the strain and magnetisation.

The results of this study were presented at the International Conference on Magnetism and Magnetic Materials (New York, 1979) and published in the Journal of Applied Physics.⁷

6. In contrast to NiO-CoO , the addition of MnO to CoO reveals a more evenly balanced contest between the anisotropies of Mn^{2+} and Co^{2+} . Unlike the single-ion behaviour of Co^{2+} , the anisotropy of Mn^{2+} depends upon multiple-ion effects, in particular the dipole-dipole interactions between the high-spin $d^5 \text{Mn}^{2+}$ ions. Our results in this system shows that the superposition of the tetragonality of CoO and the rhombohedral distortion of MnO leads to a pronounced monoclinic distortion at intermediate compositions (25 - 75% MnO). In this range, the spin direction is intermediate between that of CoO and MnO , but it is clear that

the spins are collinear at all compositions. In effect, the MoO-CoO system is similar to NiO-CoO but the consequences of the competing anisotropies are magnified by the strong anisotropy of Mn^{2+} compared with Ni^{2+} . Our neutron measurements on this system are now complete, but further refinements of our existing data are required.

7. Because of the similarity between the magnetic structures of MnO and NiO, we initially anticipated that solid solutions between them would be uneventful with collinear spins and a linear change in rhombohedral angle, α , with composition. Surprisingly, the latter expectation has not been fulfilled and samples with compositions 22, 53 and 81% MnO all appear to be essentially cubic, even at 4.2K, with collinear spins. The results are summarised below:

Cell parameters of MnO, NiO and their Solid Solutions.

NiO	$a=b=c = 2.946\text{\AA}, \alpha=\beta=\gamma = 60.20^\circ.$
$\text{Ni}_{0.78}\text{Mn}_{0.22}\text{O}$	$a=b=c = 2.995\text{\AA}, \alpha=\beta=\gamma = 60.05^\circ.$
$\text{Ni}_{0.47}\text{Mn}_{0.53}\text{O}$	$a=b=c = 3.042\text{\AA}, \alpha=\beta=\gamma = 60.04^\circ.$
$\text{Ni}_{0.19}\text{Mn}_{0.81}\text{O}$	$a=b=c = 3.098\text{\AA}, c = 3.106\text{\AA}, \alpha=\beta= 60.03^\circ, \gamma = 59.94^\circ.$
MnO	$a=b=c = 3.120\text{\AA}, \alpha=\beta=\gamma = 60.704^\circ.$

The absence of a significant rhombohedral distortion at all compositions is unexpected, but we now believe that it can be understood in terms of the nature of $\text{Mn}^{2+}\text{-Mn}^{2+}$, $\text{Ni}^{2+}\text{-Ni}^{2+}$ and $\text{Mn}^{2+}\text{-Ni}^{2+}$ exchange interactions. Whilst the homopolar interactions are certainly antiferromagnetic, it is known that the $\text{Mn}^{2+}\text{-Ni}^{2+}$ coupling is intrinsically ferromagnetic.⁸ We are presently examining the consequences of this subtlety.

8. Our investigations of the iron oxide solid solutions, FeO-MnO and FeO-CoO, are both at a preliminary stage, but some exciting results have already emerged. Despite the fact that Fe^{2+} , like Co^{2+} , has an orbitally degenerate ground state and should exhibit strong single-ion anisotropy, we have found that as little as

10% MnO is sufficient to turn the spins of Fe^{2+} through approximately 45° from [111] towards the (111) plane. In FeO-CoO, only 10% CoO is needed to pull the spin of Fe^{2+} entirely into line with that of Co^{2+} in CoO. These results are quite definitive and reveal surprisingly that the anisotropy of Fe^{2+} is weaker than that of Mn^{2+} . Our refinements of data from the FeO solid solutions have also shown that they are non-stoichiometric with defect clusters similar to those found in FeO itself. This feature makes the interpretation of the magnetic properties more complex than in the stoichiometric solid solutions.

9. When the results described in section 4 - 8 above are combined, an overall pattern begins to emerge: the strength of the anisotropy appears to fall in the sequence $\text{Co}^{2+} > \text{Mn}^{2+} \gg \text{Fe}^{2+} \sim \text{Ni}^{2+}$. This sequence differs from that found in the mixed metal fluorides K_2MF_4 where $\text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+}$. The origin of the difference requires further investigation and consideration.

We ~~have already been~~^{were} granted further access to the neutron facilities at Grenoble during summer 1980 and we are optimistic that this will continue during 1980/1.

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